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# Effect of Surfactant Headgroup on Low-Fluorine-Content $CO_2$-Philic Hybrid Surfactants

Azmi Mohamed[1,2*], Tretya Ardyani[1], Suriani Abu Bakar[2] Masanobu Sagisaka[3], Shinji Ono[3], Tsuyoshi Narumi[3], Makoto Kubota[3], Paul Brown[4], Julian Eastoe[5]

[1]*Department of Chemistry, Faculty of Science and Mathematics, Universiti Pendidikan Sultan Idris, 35900 Tanjong Malim, Perak, Malaysia*

[2] *Nanotechnology Research Centre, Faculty of Science and Mathematics, Universiti Pendidikan Sultan Idris, 35900 Tanjong Malim, Perak, Malaysia*

[3] *Department of Frontier Materials Chemistry, Graduate School of Science and Technology, Hirosaki University (Bunkyo-cho 3, Hirosaki, Aomori 036-8561, Japan*

[4] *Department of Chemical Engineering, Massachusetts Institute of Technology, 77 Massachusetts Avenue, Cambridge, Massachusetts 02139, United States*

[5] *School of Chemistry, University of Bristol, Cantock's Close, Bristol, BS8 1TS, United Kingdom*

*Corresponding author. Tel.: +601548117582; fax: +601548117296

Email address: azmi.mohamed@fsmt.upsi.edu.my

## Abstract

The article addresses an interesting issue in the development of hybrid surfactants for water-in-$CO_2$ (w/c) microemulsion stabilisation: the role of surfactant headgroup on the surfactant performance. The synthetic procedure, aqueous properties, and phase behaviour of a new hybrid sulfoglutarate surfactant are described. The compound resembles sulfosuccinate surfactants, commonly used to stabilize w/c phases, but with an extra methylene group incorporated into the hydrophilic headgroup. For comparison purposes, the related hydrocarbon (AOT14 and AOT14GLU) and fluorocarbon (di-CF2 and di-CF2GLU) surfactants are used to form w/c microemulsions. In general, the aqueous properties and w/c phase stability of both sulfoglutarates and sulfosuccinates are found to be similar, which shows the secondary role of the hydrophilic headgroup. Interestingly, the newly synthesised hybrid CF2/AOT14GLU (sodium (*4H,4H,5H,5H,5H*-pentafluoropentyl-2,2-dimethyl-1-propyl)-2-sulfoglutarate) proved to be more efficient than the normal sulfosuccinate, hybrid CF2/AOT14 ($P_{trans}$ = 383 bar, $\gamma_{cmc}$ = 26.8 mN $m^{-1}$) in terms of the aqueous behaviour and w/c phase stability. Switching to the sulfoglutarate compound, hybrid CF2/AOT14GLU ($P_{trans}$ = 232 bar, $\gamma_{cmc}$ = 20.6 mN $m^{-1}$) more effectively decreases the air-water surface tension by about ~ 5 mN $m^{-1}$ as compared to the sulfosuccinate. High-pressure phase behaviour studies show significant improvements in stabilising w/c microemulsions at much lower cloud pressures. The results indicate distinct effects of the headgroup structure on the phase behaviour and physicochemical properties, particularly for this hybrid surfactant.



Keywords: $CO_2$-philic surfactant, supercritical carbon dioxide (sc-$CO_2$), w/c microemulsions, surfactant headgroup

## 1. Introduction

Supercritical carbon dioxide is considered a desirable solvent for green material and chemical processing [1-2]. Over the past few decades supercritical carbon dioxide (sc-$CO_2$) has been used for various applications [3-4] and interest still remains high today [5-8]. As such $CO_2$ is a nonpolar molecule with low dielectric constant and solubility parameter, which makes it unsuitable for dissolving polar and high-molecular-weight materials [9]. These weak solvent properties undoubtedly limit the practical applications of sc-$CO_2$. One effective approach to overcome these problems is to use $CO_2$-philic surfactants to stabilise microemulsion phases, for example, water-in-$CO_2$ (w/c) microemulsions. The formation of reverse micelles with water pools inside bulk $CO_2$ provides a microenvironment for materials that are otherwise sparingly soluble or insoluble in $CO_2$, whereas nonpolar materials are solubilised in $CO_2$-continuous phase [10-12].

Fluorination is considered a key feature for generating $CO_2$-philic surfactants [13, 14]. An investigation using several fluorinated analogues of Aerosol-OT (AOT) shows that an increase in the level of surfactant chain fluorination the limiting air-water (a/w) aqueous surface tension ($\gamma_{cmc}$) and the w/c phase cloud pressure ($P_{trans}$)for the w/c microemulsion system [15]. However, concerns have been raised because the use of long fluorocarbon chains represents an environmental threat, and is on the decline. These issues have been successfully tackled by using low F-content hybrid surfactants, where separate fluorocarbon and hydrocarbon chains are chemically bonded to the same hydrophilic headgroup [16, 17]. This approach has driven progress generating more environmentally-responsible $CO_2$-philic surfactants.

Over the years the role of the surfactant chemical structure in w/c phase stability has been a central issue in $CO_2$ studies. Much effort has been devoted to determine how changes in surfactant molecular structure can affect physicochemical properties of aqueous surfactant solutions and w/c phase stability [13, 18-21]. A traditional concept of molecular packing

parameter (p) [22] has been widely invoked in colloid studies to explain the correlation between the molecular structure and the surfactant self-assembly. This geometric parameter is defined as p= $v_0 / a_e l_0$ and includes the contributions of the volume ($v_0$) and length ($l_0$) of the surfactant tail and the interfacial area each surfactant molecule occupies ($a_e$) (which is referred to as the headgroup area in most cases).

Regarding the volume and length of the surfactant tails, studies using double chain anionic surfactants have been devoted to the effect of structural modifications on the surfactant chain with limited surface tension ability, w/c phase stability, and surfactant solubilising power [15, 23-27]. Branching, methylation, and fluorination of the chain tips have been shown to decrease intermolecular interactions between the surfactant tails and produce more favourable tail-$CO_2$ interactions which improve the $CO_2$ compatibility [28, 29]. A recent study on low fluorine content hybrid surfactants has shown that for a constant headgroup type and fluorocarbon chain structure the surfactant performance is notably affected by modification of the hydrocarbon $CO_2$-philic chain structure. Trends in hydrophobicity, the limiting molecular area at the aqueous phase cmc $A_{cmc}$, and w/c phase stability were found to link closely with the degree of chain branching, and this can be ranked using and empirical branching factor [30]. A convenient way to rank the effectiveness of surfactants in w/c systems is using the molar solubilization ratio *w* = [water]/[surfactant]: under equivalent P and T conditions, the higher *w* the more effective the surfactant. Meanwhile, changes of the hydrophilic headgroup chemical structure have not been systemically studied, mainly because of a lack of suitable compounds; hence, most studies focused on the effects of counterions and headgroup polarity [31-34]. The most relevant work [15, 23, 35] investigated glutarate analogues of the normal sulfosuccinate surfactant.

Previously, sulfoglutarate surfactants (denoted as GLU) were obtained using fluorinated AOT-analogues, for example sodium bis (*1H, 1H, 5H*-octafluoropentyl)-2-

sulfosuccinate (di-HCF4; $\gamma_{cmc}$ = 26.8 mN $m^{-1}$, $P_{trans}$ = 193 bar; *w* = 10 at 25°C) and the related compound sodium bis (*1H, 1H, 5H*-octafluoropentyl)-2-sulfoglutaconate (di-HCF4GLU; $\gamma_{cmc}$ = 25.4 mN $m^{-1}$, $P_{trans}$ = 181 bar; *w* = 10 at 25°C) [15, 23]. In fact, changing sulfosuccinate headgroup for sulfoglutarate increases the hydrophobicity and surface-tension-lowering ability, whereas only a subtle change on the area per surfactant headgroup on the cmc ($A_{cmc}$) is observed. Later observations noted a slight enhancement of the w/c phase stability with the sulfoglutarate surfactant. Another highly interesting observation with sulfoglutarate surfactants was reported by Sagisaka et al. [36-39] using two related compounds: sulfosuccinate nFS$(EO)_2$ and sulfoglutarate nFG$(EO)_2$ (n = 4, 6, 8). Visual observation and UV-Visible measurements, with the probe dye methyl orange (MO) as a tracer, showed that sulfoglutarate attains higher solubilising power in $CO_2$ than the sulfosuccinates. Moreover, 4FG$(EO)_2$ (sodium 1,5 bis [(*1H, 1H, 2H, 2H*-perfluorohexyl)oxy]-1,5-dioxopentane-2-sulfonate) has the highest solubilising power *w* reported to date (*w* ~ 80), which is a significant improvement over other known $CO_2$-philic surfactants.

In terms of hydrocarbon surfactants, only a few studies have been reported. Using the glutarate analogues of AOT and di-C6SS, which are denoted as AOTGLU and di-C6GLU, respectively, Nave et al. [35] showed that sulfoglutarate and sulfosuccinate surfactants have notably similar aqueous properties, e.g., critical micelle concentration, cmc, $\gamma_{cmc}$ and microemulsion phase stability. More recently, Sagisaka et al. [29] also reported the effect ofan additional –$CH_2$- spacer on surfactant solution physicochemical properties with two series of highly branched AOT analogue surfactants: di-$BC_nSS$ (sulfosuccinate type) and di-$BC_nSG$ (sulfoglutarate type). In most cases, for hydrocarbon surfactants a modification of the hydrophilic headgroup exerts a weaker effect on the limiting surface tension than for analogous fluorinated surfactants.

The results prompt an interesting question: “what if the similar strategy is applied to hybrid surfactants?”. To address this issue, the glutarate analogue of the hybrid sulfosuccinate surfactant was synthesized, and the performance was investigated. To minimize the fluorination, in this work, the fluorocarbon chain of the hybrid surfactant was fixed using the low-fluorine-content di-CF2 tail [40], whereas the hydrocarbon chain is an AOT14 tail (Table 1), which is the di-chain analogue of the $CO_2$-soluble tri-chain TC14 (sodium 1,4-bis(neopentyloxy)-3-(neopentyloxycarbonyl)-1,4-dioxobutane-2-sulfonate) surfactant [41]. For comparison purposes, the performance of the related hydrocarbon and fluorinated surfactants are included. The chemical structures of hybrid, hydrocarbon, and fluorinated sulfoglutarate surfactants, which are denoted as hybrid CF2/AOT14GLU, AOT14GLU, and di-CF2GLU, respectively, and its normal sulfosuccinate, are provided in Table 1. As observed, sulfosuccinates and sulfoglutarates differ in only the headgroup structures: with the addition of an extra $–CH_2-$ spacer on the hydrophilic part, sulfoglutarate surfactants have a symmetrical headgroup with respect to the $–SO_3Na$ function.

The development of $CO_2$-philic surfactants represents a considerable chemical challenge, but significant progress has been made to untangle the structural requirements for $CO_2$-philicity. Here, apparently subtle changes in the hydrophilic headgroup can help optimize the surfactant structure, in particular to attain a minimum amount of fluorine while retaining good performance in $CO_2$. This study provides new information on how the hydrophilic-headgroup influences surfactant performance in w/c systems, particularly regarding hybrid surfactants, and fuels research into low-fluorine-content $CO_2$-philic surfactants.

## 2. Experimental section

### *2.1 Materials*

Synthesis of sulfosuccinate surfactants was previously reported [40, 42]. Sulfoglutarate surfactants were prepared using the same alcohol precursors as used for sulfosuccinate surfactants. The fluorinated and hydrocarbon sulfoglutarate surfactants were synthesised using a Dean and Stark apparatus as shown in a previous work [39]. Meanwhile, an additional esterification step was included to obtain the hybrid sulfoglutarate surfactant. Further information on the hybrid-sulfoglutarate-surfactant synthesis can be found in section 2.2. Dimethyl glutaconate ≥ 97% (Sigma Aldrich) was used without further treatment. Distilled water (Otsuka Pharmaceutical, injection grade, pH = 6.5) and pure $CO_2$ (Tomoe Shokai, 99.99%) were used as received.

### *2.2 Surfactant synthesis*

#### *2.2.1 Synthesis of hybrid CF2/AOT14GLU diester*

A mixture of dimethyl glutaconate (1.0 eq), 4*H*,4*H*,5*H*,5*H*,5*H* – pentafluoropentanol (1.0 eq), and *p*-toluene sulfonic acid monohydrate (0.1 eq) in toluene (100 ml/5 g dimethyl glutaconate) was reacted overnight under reflux to produce the fluorinated monoester. During the transesterification reaction, methanol was azeotropically liberated to shift the reaction equilibrium and used as an indicator for the reaction completion. After the reaction was considered complete, the CF2-monoester was washed with warm water (70°C). The fluorinated monoester was obtained as yellow transparent liquid after the solvent removal using a rotary evaporator.

To produce the hybrid CF2/AOT14GLU diester, CF2-monoester (1.0 eq) and 2,2-dimethyl propanol (1.0 eq) were dissolved in toluene (10 ml/g monoester) in the presence of *p*-toluene sulfonic monohydrate (0.1 eq). The reaction was performed overnight to remove

methanol as a result of the transesterification reaction. Then, the hybrid CF2/AOT14GLU diester was cooled to 70ºC and repeatedly washed with warm water to remove the unreacted *p*-toluene sulfonic monohydrate. The brown crude diester was obtained by rotary evaporation.

### *2.2.2 Synthesis of the hybrid CF2/AOT14GLU surfactant*

The crude hybrid CF2/AOT14GLU diester (1.0 eq) was dissolved in ethanol (100 ml), and water was added to the mixture until saturation. After sodium hydrogen sulfite (4.0 eq) was added, the reaction mixture was refluxed for 72 h. The reaction was monitored using TLC eluted with ethyl acetate and considered complete when the diester spot (Rf ~ 0.9) disappeared. The product formation was indicated by the appearance of the baseline surfactant spot (Rf ~ 0). The solvents were evaporated, and a white crude surfactant remained, which was left to dry overnight in an oven at 70°C. Then, the crude surfactant was dissolved in dried acetone and centrifuged to remove any remaining inorganic impurity from the sulfonation step. The pure surfactant was obtained as a white yellowish powder after drying in an oven overnight at 60°C (average yield = 40%).

**Hybrid CF2/AOT14GLU**

$^{1}$H NMR (500 MHz, $CDCl_3$, TMS), ($\delta_H$/ppm): 0.88–0.97 (a, s, 9H), 1.86–1.99 (b, m, 2H), 2.08–2.19 (c, m, 2H), 2.56–2.72 (d, m, 2H), 2.98–3.11 (e, m, 2H), 3.70–3.82 (f, m, 4H), 4.08–4.22 (g, m, 1H). Elemental analysis: found C, 36.46; H, 5.17; S, 6.30. Calcd C, 38.80; H, 4.78; S, 6.90.

**di-CF2GLU**

$^{1}$H NMR (500 MHz, $(CD_3)_2CO$, TMS), ($\delta_H$/ppm): 1.92–1.98 (a, m, 4H), 2.26–2.37 (b, m, 4H), 2.97 (c, s, 4H), 3.62–3.3.71 (d, m, 4H), 4.19–4.26 (e, m, 1H). Elemental analysis: found C, 32.77; H, 2.58; S, 6.17. Calcd C, 32.50; H, 3.09; S, 5.78.

**AOT14GLU**

$^{1}$H NMR (500 MHz, $(CD_3)_2CO$, TMS), ($\delta_H$/ppm): 0.88–0.94 (a, t, 18H, *J* = 14.85 Hz), 2.66–2.70 (b, dd, 4H, *J* = 6.85, 16.6 Hz), 3.76–3.78 (c, d, 4H, *J* = 10.3 Hz), 3.80–3.82 (d, s, 1H). Elemental analysis: found C, 44.59; H, 7.12; S, 9.35. Calcd C, 48.12; H, 7.27; S, 8.56.

### *2.3 Surface tension measurements*

The air-water (a/w) surface tensions were measured using a Wilhelmy tensiometer (CBVP-A3, Kyowa Interface Science), which was equipped with a platinum plate. All measurements were performed at 25°C until the surface tension of the aqueous surfactant solutions reached constant values. Detailed information of the experimental procedures and apparatus are described elsewhere [36, 43]. The critical micelle concentrations (cmc) of each surfactant solution were obtained from the intersection of the graph of the surface tension ($\gamma$) versus ln of concentration (ln c).

### *2.4 High-pressure phase behaviour and UV-Visible absorption measurement*

The changes in phase stability of the surfactant/water/$CO_2$ mixtures were visually observed at constant composition with varying temperature and pressure. The measurements were performed at pressures up to 400 bar and controlled temperatures ranging over 35-75°C. To obtain comparable results, the surfactant concentration was fixed at 0.05 mol $dm^{-3}$. Meanwhile, to examine the aqueous core formation in w/c microemulsion, UV-Visible absorption spectroscopy measurement with the probe dye methyl orange (MO) solution was performed. The temperature, pressure, surfactant and MO concentration were fixed at 45°C, 400 bar, 0.05 mol $dm^{-3}$ and 0.1 wt % in water, respectively. Predetermined amounts of surfactants and $CO_2$ were loaded into a variable-volume high-pressure optical cell. Then, water or MO solution was added to the surfactant/$CO_2$ mixture until clear Winsor IV microemulsions

became turbid macroemulsions. Further information about the experimental procedures and apparatus can be found elsewhere [37, 44].

## 3. RESULTS AND DISCUSSION

### *3.1 Air-water (a/w) surface tension measurement*

**Cmc's**. Figure 1 shows the aqueous surface tension data of sulfosuccinate and sulfoglutarate surfactants at 25°C as a function of surfactant concentration. Meanwhile, the aqueous properties of each surfactant, which were derived from the surface tension measurement, are shown in Table 2. Previously [23, 29, 35], with several glutarate analogues of fluorinated and hydrocarbon surfactants, it has been shown that the cmc decreases after the $–CH_2$ spacer is added to the surfactant hydrophilic headgroup. However, the decreasing cmc following hydrophilic-headgroup modification does not always follow this simple pattern because methylene and methyl groups that are added to the surfactant do not contribute equally [45]. Here, the comparisons of individual cmc between sulfoglutarate and normal sulfosuccinate for the three surfactant classes show the trend of increasing cmc when the headgroup architecture was changed (see Table 2). It is postulated that micelle formation is a result of the balance in tail-water and headgroup-water interactions. Although the tails favour aggregation the headgroup remains hydrated [22, 46].

**Limiting surface tension**. One important function of the surfactant is the ability to decrease the air-water surface tension to the limiting value $\gamma_{cmc}$, and this value importantly represents the surfactant effectiveness and is a property of interest for the approximation of w/c microemulsions [15]. Notice that the $\gamma_{cmc}$ values of each surfactant are essentially similar for all surfactants considered (see Table 2). The differences are highly likely within experimental uncertainties ($\pm$ 1 mN $m^{-1}$). Thus, the addition of the $–CH_2$ group on the hydrophilic part exerts

much less effect than if it would be placed in the alkyl chain instead [34, 47]. Table 2 shows that the extra $–CH_2$- content in the hydrophilic group does not increase the overall surfactant hydrophobicity. In contrast, a prior study that used a series of linear di-chain sulfosuccinates, di-C*n*SS (n = 4 - 8), showed that the cmc of surfactants reduced to approximately three fourths for each $–CH_2$ that was added to the surfactant chain [47]. In addition, the increase in total carbon number by adding $–CH_2$ to the surfactant chain is believed to contribute to the ability of a surfactant in reducing the air-water surface tension [34, 47]. However, the obtained data show one unexpected finding for low-surface-energy materials. The hybrid CF2/AOT14GLU exhibits a notably low $\gamma_{cmc}$ (down to 20.6 mN $m^{-1}$), which is even lower than the fully fluorinated surfactant di-CF2GLU ($\gamma_{cmc}$ = 21.8 mN $m^{-1}$). This result is interesting because a double fluorocarbon (FC)-tail surfactant usually has a greater surface-tension-lowering ability than a single FC-tail one of the same FC length, and the $\gamma_{cmc}$ value of the hybrid CF2/AOT14GLU was expected to be between those of di-CF2GLU and AOT14GLU. It may be expected that the ability of the hybrid CF2/AOT14GLU to stabilise w/c microemulsions is enhanced because this surfactant also proves to be notably efficient in decreasing air-water surface tension.

**Surfactant coverage at the a/w interface.** One important parameter to characterise the area occupied by the surfactant molecule is the effective area per headgroup at the respective cmc ($A_{cmc}$/$Å^2$). The pre-cmc data were fitted to quadratics to generate adsorption isotherms using Gibbs equation (Eq. 1); thus, the area per headgroup at the cmc ($A_{cmc}$) was calculated. The prefactor m = 2 is responsible for the ratio 1:1 of dissociating ions for ionic surfactants.

$$\Gamma = -\frac{1}{mRT}\frac{d\gamma}{d\ln c} \qquad (1)$$

$$A_{cmc} = \frac{1}{\Gamma N_A} \qquad (2)$$

For all cases, the sulfoglutarate surfactants exhibit notably larger $A_{cmc}$ than sulfosuccinates, which follows the similar observed trends for hydrocarbon and fluorinated sulfoglutarate surfactants in previous publications [29, 35, 38]. Considering that these two surfactant classes differ only in headgroup architecture, the changes in $A_{cmc}$ can be ascribed to the effect of adding an extra $–CH_2^-$ to the surfactant hydrophilic part. Because of the presence of the $–CH_2^-$ spacer in the surfactant headgroup, the glutarate surfactants have slightly larger headgroups [48]. Moreover, the double tails of the sulfoglutarate surfactant may be more open than those of the sulfosuccinates because of the extra linking spacer in the hydrophilic group [29, 35, 36]. These factors may cause the sulfoglutarate surfactants at the interface to occupy larger areas.

### *3.2 High-pressure phase behaviour*

In $CO_2$ studies, high-pressure phase behaviour is necessary to seek the optimum conditions for stabilizing water-in-$CO_2$ microemulsions. Here, to readily compare the performance of all surfactants, a fixed surfactant concentration and water-to-surfactant molar ratio (*w*) were used. The phase behaviour and $P_{trans}$ value of the surfactants in this study are shown in Figure 2 and Table 2, respectively. $P_{trans}$ is the lowest pressure for a given composition and temperature at which the microemulsions remain with the single transparent one phase (1Φ), and $P_{trans}$ was used to evaluate the ability of a $CO_2$-philic surfactant to stabilise w/c microemulsions. Below $P_{trans}$, phase separation occurs and the mixtures become turbid, which indicates the formation of macroemulsions (2Φ).

Attempts to disperse water in dense $CO_2$ using both sulfosuccinate and sulfoglutarate versions of hydrocarbon surfactants (AOT14 and AOT14GLU) did not produce single transparent phases under the experimental conditions used here. Hence, the data for these two surfactants are not included in the phase diagram. Earlier studies on the identical system also reported the inability of the AOT14 surfactant to stabilise w/c microemulsions [42] despite the

versatility of the parent AOT14; which is the TC14 surfactant, in a wide range of solvent [41, 49]. However, changing the hydrophilic headgroup into the larger sulfoglutarate was not sufficient to increase the tendency of the surfactants to stabilize w/c microemulsions. Certainly, this study is the first on the performance of hydrocarbon sulfoglutarate surfactants in $CO_2$. Previous work that used hydrocarbon sulfoglutarate surfactants focused on water-in-oil (w/o) microemulsion system and low-surface-energy materials [29, 35].

As expected, the fully fluorinated surfactant di-CF2 exhibits the lowest cloud pressure among the surfactants investigated in this study. Fluorination on the surfactant chains is known to be the key factor for producing a favourable quadrupolar interactions between the surfactant tails and $CO_2$; thus, a fluorinated surfactants attain the lowest cloud pressures [14, 15, 40]. Here, the use of the sulfoglutarate surfactant di-CF2GLU increases $P_{trans}$ by approximately 30 bar at 55°C. However, the difference is small, considering the uncertainties of approximately 20-40 bar. Earlier studies by Sagisaka et al. [37, 38] also reported the minor difference in $P_{trans}$ when exchanging sulfosuccinate with the sulfoglutarate headgroup for all examined fluorinated surfactants.

For hybrid surfactants, exchanging sulfosuccinate with the sulfoglutarate headgroup significantly affects the stabilization of the w/c microemulsion systems. Compared with the hybrid CF2/AOT14 ($P_{trans}$ = 383 bar), the extra $–CH_2$ content on the hybrid CF2/AOT14GLU ($P_{trans}$ = 232 bar) decreases $P_{trans}$ to approximately 150 bar at 55°C, which even approaches the level of the fluorinated surfactant di-CF2 (219 bar). The significant improvement of the hybrid CF2/AOT14GLU may be related to high interfacial activity at the water-$CO_2$ interface. Returning to the data of $\gamma_{cmc}$ in Table 2, the hybrid CF2/AOT14GLU exhibits the lowest values, which illustrates the high effectivity in reducing the air-water surface tension and consequently the water-$CO_2$ interfacial tension [36]. This result is consistent with the arguments in [15],

suggesting that surfactants with lower $\gamma_{cmc}$ will be expected to stabilise w/c microemulsions formation at lower $P_{trans}$ values.

### *3.3 UV-Visible spectroscopy measurement of w/c microemulsions*

To gain evidence for w/c microemulsion formation, the presence of reverse micelles in sc-$CO_2$ was shown by determining the incorporation a polar water-soluble probe dye methyl orange (MO) in the water/surfactant/$CO_2$ systems. (MO is insoluble in sc-$CO_2$ and soluble in water.) The existence of reverse micelles in sc-$CO_2$ is indicated by the red dyed single-phase mixtures because the MO dissolves inside surfactant-stabilized water pools of the $CO_2$ continuous phase [44]. The UV-visible absorption spectra of MO in the water/surfactant/$CO_2$ systems are shown in Figure 3. With the aforementioned phase behaviour studies, the fluorinated surfactants di-CF2 exhibit the highest and MO broad peak absorbance. The comparisons among hybrid surfactants show that the sulfoglutarate version provides better $CO_2$-compatibility, as reflected by the higher absorbance of the hybrid CF2/AOT14GLU.

The solubilisation of MO in water-$CO_2$ microemulsions is expected to display a linear relationship for MO absorbance and *w* up to a certain *w* value, as shown in Figure 4. As observed, the increase in *w* gradually decreases, which suggests the phase transition from Winsor IV (1Φ) to Winsor II (2Φ) microemulsions. Following the similar lines [36-38], the trend of increasing solubilising power is also observed when sulfosuccinate is changed for sulfoglutarate. It has been previously noted that for a $CO_2$-philic surfactant to have high solubilising power, structural disorder in the surfactant molecular structure is required to decrease the length-to-breadth ratio, which decreases the possibility of liquid-crystal-like formation [36, 50]. Although $w_{max}$ is larger for the nFG$(EO)_2$ series [36-38], here, the sulfoglutarate version provides slightly higher solubilising power than the normal sulfosuccinates di-CF2 ($w_{max}$ = 10) and hybrid CF2/AOT14 ($w_{max}$ = 3). Usind the sulfoglutarate

surfactant increases the solubilising power of di-CF2GLU and hybrid CF2/AOT14GLU to $w_{max}$ = 13 and $w_{max}$ = 7, respectively. Recalling the phase behaviour results, instead of enhancing the surfactant solubilising power, swapping sulfosuccinate for the sulfoglutarate headgroup affects the surfactant efficiency in stabilising the w/c microemulsion more, particularly with the hybrid surfactant.

## 4. Conclusions

There is currently great interest in understanding the role of surfactant molecular structure on w/c phase formation and stability. For decades, extensive studies were devoted to define the effect of the surfactant tail architecture [13, 15, 24, 50, 51]. However, only few works have alluded to the effects of hydrophilic-headgroup modifications on surfactant performance in $CO_2$ [36, 38, 39].

To further explore the molecular design requirements for $CO_2$-philic surfactants, three classes of custom-made AOT-derived surfactant–sulfoglutarate surfactants were successfully synthesised. Although some surfactants such as di-CF2 and AOT14 were previously investigated, the others are new. It is important to note that this study is the first time that these sulfoglutarate surfactants (hydrocarbon, fluorinated, and hybrid) have been compared in terms of surface tension behaviour and w/c phase stability. All results show that the extra $–CH_2$ content in the surfactant headgroup causes different effects for different surfactant types. The differences in $P_{trans}$ and $\gamma_{cmc}$ are indeed subtle considering the involved uncertainties. Conversely, a significant $–CH_2$ head group spacer effect was observed for the hybrid surfactants. The hybrid CF2/AOT14GLU is more $CO_2$-philic than the parent hybrid CF2/AOT14 as indicated by the lower $P_{trans}$ and $\gamma_{cmc}$ values. Apparently, it is clear that not all $–CH_2$ groups that are added to the hydrophilic headgroup contribute equally to the surfactant $CO_2$-philicity. Further investigations are necessary to unravel the remaining question: “how

does this modification on the surfactant headgroup have a significantly different effect on the surfactant performance in w/c microemulsions?" Importantly, the obtained results may be used as a reference to design a new generation of low-fluorine-content-based $CO_2$-philic surfactants.

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